

## Research Article

# N-Heterocyclic Germylenes: Structural Characterisation of Some Heavy Analogues of the Ubiquitous N-Heterocyclic Carbenes

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The X-ray crystal structures of three N-heterocyclic germylenes (NHGes) have been elucidated including the previously unknown 1,3-bis(2,6-dimethylphenyl)diazagermol-2-ylidene (**1**). In addition, the X-ray crystal structures of the previously synthesised 1,3-bis(2,4,6-trimethylphenyl)diazagermol-2-ylidene (**2**) and 1,3-bis(2,6-diisopropylphenyl)diazagermol-2-ylidene (**3**) are also reported. The discrete molecular structures of compounds **1** to **3** are comparable, with Ge-N bond lengths in the range 1.835–1.875 Å, while the N-Ge-N bond angles range between 83.6 and 85.2°. Compound **2** was compared to the analogous N-heterocyclic carbene species, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). The major geometrical difference observed, as expected, was the bond angle around the divalent group 14 atom. The N-Ge-N bond angle was 83.6° for compound **2** versus the N-C-N bond angle of 101.4° for IMes. The Sn equivalent of (**1**), 1,3-bis(2,6-dimethylphenyl)diazastannol-2-ylidene (**4**), has also been synthesised and its crystal structure is reported here. In order to test their suitability as ligands, compounds **1** to **3** were reacted with a wide range of transition metal complexes. No NHGes containing metal complexes were observed. In all cases the NHGe either degraded or gave no reaction.

## 1. Introduction

The meteoric rise of the N-heterocyclic carbene (NHC) ligand family over the past 25 years has been remarkable with the ligands dominating the organometallic chemistry landscape. In particular, the carbenes based on the imidazol-2-ylidene framework, first reported by Arduengo et al., have proven highly successful [1]. Their synthetic utility shows no sign of abating, with NHC ligands standing firm in the field of transition metal catalysis while also breaking new ground in the field of organocatalysis [2]. Their success in transition metal catalysis has been largely down to their ability to form strong  $\sigma$ -bonds with transition metals while the “bottleneckability” of a number of NHCs has allowed them to be deployed in organocatalysis. In comparison, the heavier direct analogues of the NHCs, namely, the N-heterocyclic silylenes, germylenes, stannyls, and plumbylenes, have received considerably less attention. Reports on the chemistry of the N-heterocyclic germylenes (NHGes) in particular are

relatively sparse [3–6]. Three distinct classes of NHGes are known (Figure 1), and these are (i) unsaturated nonanellated, (ii) saturated nonanellated, and (iii) anellated. There have been a number of different anellated backbones reported including benzene [7], naphthalene [8], and phenanthrene [9]. Furthermore bisanellated [10] and macrocyclic [11] examples have also been reported. Complementing the reports of various NHGes and related complexes are a number of theoretical studies. Noteworthy are reports by Hitchcock et al. [12] and Tuononen et al. [13] which examined the electronic structures of main-group carbene analogues. Additionally Szivási et al. have assessed the ligating abilities of NHGes [14].

The chemistry of the nonanellated NHGes is limited, with only eight NHGes, six transition metal complexes, and three s-block metal complexes reported to date. The majority of the transition metal complexes are zero valent complexes of nickel and molybdenum. Hermann et al. reported the synthesis of two nickel carbonyl complexes from the reaction

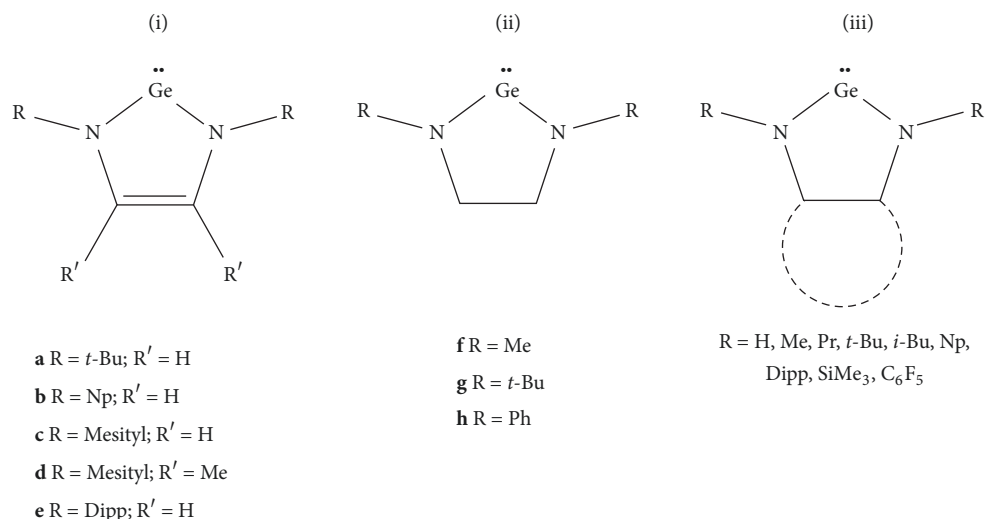


FIGURE 1: Previously reported NHGes.

of  $\text{Ni}(\text{CO})_4$  and the saturated *t*-Bu ligand (Figure 1, **g**) [15]. Both  $[\text{Ni}(\text{CO})_3(\text{NHGe})]$  and  $[\text{Ni}(\text{CO})_2(\text{NHGe})_2]$  were obtained. In addition the homoleptic species,  $[\text{Ni}(\text{NHGe})_3]$ , could be prepared when the same ligand was reacted with  $[\text{Ni}(1,5\text{-cod})_2]$ . Kühl et al. reported the synthesis of molybdenum carbonyl complexes from the reaction of  $[\text{Mo}(\text{CO})_4(\text{NCET})_2]$  and the unsaturated Np ligand (Figure 1, **b**) [16]. The principal species formed was  $[\text{Mo}(\text{CO})_4(\text{NHGe})_2]$ ; however, the only X-ray crystal structure reported was for  $[\text{Mo}(\text{CO})_3(\text{NHGe})_3]$ , which formed alongside the bis-NHGe species. The exception to the zero valent complexes is the copper(I)  $\beta$ -diketiminate complex,  $[\text{Cu}(\text{L}^{\text{Me}_2})(\text{NHGe})]$  ( $\text{L}^{\text{Me}_2} = \beta$ -diketiminate), reported by Tolman et al. [17]. This complex was prepared through the reaction of the unsaturated mesityl ligand (Figure 1, **c**) with a copper(I) bis( $\beta$ -diketiminate) complex. Blom et al. reported the first s-block metal complexes bearing NHGe ligands [18]. Three alkaline-earth-metal complexes with the general formula  $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{NHGe})]$  ( $\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$ ) were prepared utilizing the unsaturated *t*-Bu ligand (Figure 1, **a**). Only the calcium complex was characterised by X-ray crystallography, with the asymmetric unit additionally containing a second molecule which was identified as the decomposition product of the NHGe complex. We were interested in exploring the chemistry of the germylene analogues of the “classical” bulky NHC ligands, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), and 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene (IXy). The initial aim was to structurally characterise the NHGes, since these details were absent from the literature, before assessing their synthetic utility. Herein, we report the structural characterisation of three unsaturated NHGes and we also discuss our efforts to realise the potential of these species as synthetically useful ligands. In addition we report the structural characterisation of a new unsaturated N-heterocyclic stannylene (NHSn).

## 2. Results and Discussion

The preparation of the NHGes is synthetically straightforward, via a two-step synthesis, following the synthetic protocols initially outlined by Herrmann et al. [15] and latterly by Tolman et al. [17]. The first step involves the lithiation of the required diimine in THF. This is followed by the addition of a stoichiometric amount of  $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$ , which, after extraction into *n*-hexane, results in the isolation of pure NHGe. Crystals suitable for single-crystal X-ray crystallography studies were grown from concentrated *n*-hexane solutions of the relevant NHGe. We successfully prepared and characterised three NHGes, namely, 1,3-bis(2,6-dimethylphenyl)diazagermol-2-ylidene (**1**), 1,3-bis(2,4,6-trimethylphenyl)diazagermol-2-ylidene (**2**), and 1,3-bis(2,6-diisopropylphenyl)diazagermol-2-ylidene (**3**). All ligands were isolated in moderate yields as yellow/orange solids.  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_{12}$  revealed the purity of all three species to be high, with no evidence of any other species in solution. For all three species the characteristic chemical shift values observed for the unsaturated backbone of the heterocycle were in the range 6.59–6.64 ppm, consistent with previous reports [17, 19]. The synthesis of species **2** and **3** has previously been reported but no structural study has been published. In the case of **3**, Jones et al. reported that a badly disordered structure was obtained and consequently the data was not discussed [19]. Disorder in other  $\text{XN}_2\text{C}_2$  rings, where X is a heavy group 14 element, is a common structural feature with the heavy X atom often apparently disordered by a  $180^\circ$  rotation about an axis passing through both N atoms [20–22]. Despite small amounts of apparent disorder, the structures of **1** and **2** are of good quality. The dataset for ligand **3** was problematic, despite repeated collection of data from differing sets of crystals. However we have obtained a structure, where the disorder is well modelled and consequently the general structural parameters can be discussed.

TABLE 1: Summary of key structural parameters for compounds **1** to **3**.

	Compound <b>1</b>	Compound <b>2</b>	Compound <b>3</b>
Ge-N [Å]	1.862(2)	1.861(3)	1.835(4)
	1.869(2)	1.875(4)	1.861(4)
N-Ge-N [°]	83.74(10)	83.55(16)	85.2(2)
C <sub>ar</sub> -N-Ge [°]	125.53(17)	125.2(3)	130.2(3)
	126.86(18)	126.2(3)	131.0(4)
C <sub>het</sub> -N-Ge [°]	114.48(19)	112.7(3)	113.1(5)
	113.6(2)	113.9(3)	114.8(4)

The X-ray structure of **1** is shown in Figure 2 and it is clear that the core 5-membered ring is planar. The structure of **1** is isostructural with the previously reported N-heterocyclic silylene analogue [23].

The Ge-N bond lengths for **1** are 1.862(2) and 1.869(2) Å while the N-Ge-N bond angle is 83.74(10)°. The X-ray structure of **2** is shown in Figure 3 and shares the same gross features as **1**. The Ge-N bond lengths in **2** are 1.861(3) and 1.875(4) Å while the N-Ge-N bond angle is 83.55(16)°. While the bonding parameters for compounds **1** and **2** do not warrant further comparison, the comparison of the structure obtained for compound **2** with its NHC analogue IMes is of interest. Of significance is the differing bond angle observed around the divalent group 14 atom in **2** versus the analogous IMes ligand [83.55(16)° vs. 101.4(2)°]. In contrast all other angles compare relatively well to the equivalent angles reported for the IMes structure [24]. It is apparent that the steric strain within the 5-membered ring will be greater for **2** than for IMes. As both **2** and IMes have N-X-N angles that are fairly typical of the N-Ge-N and N-C-N species, respectively, this observation regarding strain can be expanded to become a general comment for NHGes. Selected bond lengths and angles for **1** and **2** are given in Table 1.

While the discrete structures of **1** and **2** are essentially analogous there are some interesting differences when the extended structures are compared. Compound **1** displays a number of weak intermolecular interactions. Of note are the C-H...C interactions between hydrogen atoms of the heterocycle and carbon atoms of a C<sub>6</sub> aromatic ring. These R<sup>2</sup><sub>2</sub>(10) motifs form centrosymmetric dimeric pairs of molecules. The H...C distance measures 2.87 Å, well within the sum of the van der Waals radii. The remaining C<sub>6</sub> ring forms a relatively long range (shortest C...C distance 3.798 Å) and centrosymmetric  $\pi$ - $\pi$  interaction with the same ring of a neighbouring molecule. Together these two interaction types result in a 1D supramolecular chain motif with the molecules arranged in a head-to-tail manner. Compound **2** exhibits a similar dimeric motif with centrosymmetric R<sup>2</sup><sub>2</sub>(10) C-H...C interactions between hydrogen atoms of the heterocycles and carbon atoms of neighbouring C<sub>6</sub> aromatic rings. The closest H...C contacts are shorter than in **1**, at 2.72 Å. As in **1**, the remaining C<sub>6</sub> aromatic ring approximates a  $\pi$ - $\pi$  interaction, but here the ring-to-ring overlap has been further displaced so that the shortest C...C contact now involves the C atom of a Me group rather than of the ring. In addition, there is a further weak intermolecular interaction between the

germanium centre and a hydrogen atom of a methyl group in a neighbouring molecule. The Ge...H distance is 3.12 Å (Figure 4). There are no similar Ge...H contacts at less than the sum of the van der Waals radii in **1**. The structure of the carbene analogue of **2**, IMes, provides some contrasting supramolecular features [24]. In **2** both mesityl rings are involved in R<sup>2</sup><sub>2</sub>(10) C-H...C interactions. Additionally, the carbenic carbon interacts with not one but two methyl groups of two neighbouring molecules, both with C...H distances less than the sum of the van der Waals radii, 2.72 and 2.90 Å.

The X-ray crystal structure for compound **3** was determined but as mentioned previously was disordered. However, the data has been modelled well allowing us to discuss some basic parameters of the discrete molecular structure. Both the Ge-N bond lengths and N-Ge-N bond angle are consistent with the values observed for compounds **1** and **2**. The Ge-N bond lengths measure 1.835(4) and 1.861(4) Å while the N-Ge-N bond angle is 85.2(2)°. The X-ray crystal structure is shown in Figure 5 while selected bond lengths and angles are shown in Table 1.

During this study the X-ray crystal structure of the related NHSn species, 1,3-bis(2,6-dimethylphenyl)diazastannol-2-ylidene (**4**), was elucidated. This species was generated via the reaction of the diimine with SnCl<sub>2</sub>·1,4-dioxane, under analogous conditions to those used to prepare the NHGe species. Unfortunately this X-ray structure (Figure 6) also exhibits significant disorder in the heavy atom positions therefore limiting what can be sensibly discussed. The structure contains two crystallographically independent fragments, one of which is disordered about a crystallographic centre of symmetry,  $Z' = 1.5$ . Compared with the values for the Ge species in Table 1, the X-N bond lengths are of course longer (1.973(4) to 2.087(3) Å) and this leads to more acute N-X-N angles (78.08(11) and 80.54(15)°). The conformations of the major disorder components of the two independent molecules of **4** differ slightly with respect to the angles formed between the planes of the C<sub>6</sub> aromatic rings and the planes of the heterocycles. The conformation of one molecule has one perpendicular C<sub>6</sub> ring and one C<sub>6</sub> ring that is twisted over 15° from the perpendicular, whereas for the centrosymmetric molecule both C<sub>6</sub> rings lie approximately 14° from the perpendicular.

Having successfully characterised three NHGes by X-ray crystallography the focus of the research shifted to establishing their effectiveness as ligands in coordination chemistry. A number of reactions were attempted with a range of transition

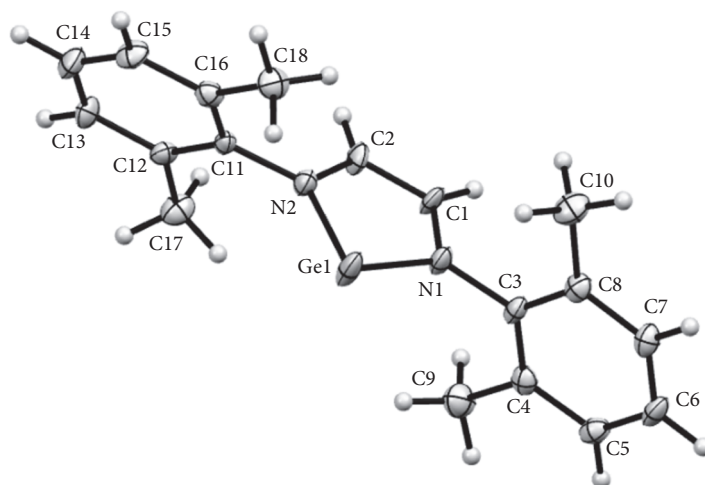


FIGURE 2: Molecular structure of **1**. Here, and in all subsequent displacement ellipsoid plots, non-H atoms are drawn as ellipsoids at the 50 % probability level and H atoms are drawn as small spheres of arbitrary size. The minor disorder component (sof 3%) is not shown.

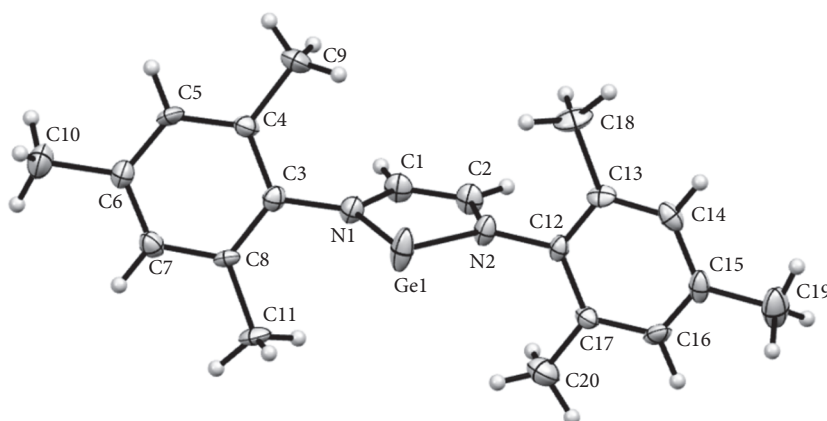


FIGURE 3: Displacement ellipsoid representation of the molecular structure of **2**.

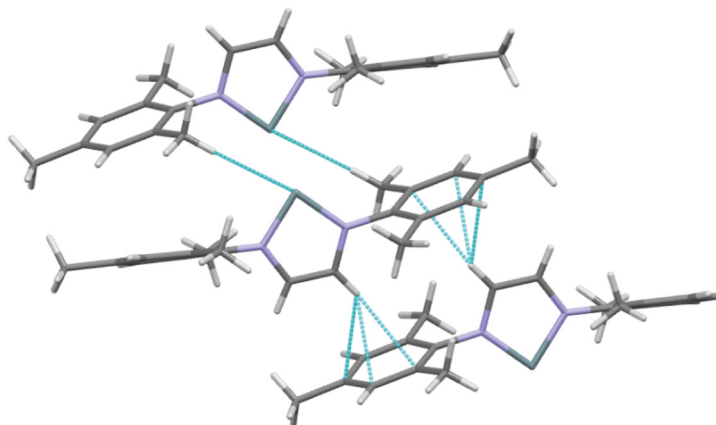


FIGURE 4: Part of the extended structure of **2** showing short C-H...C and C-H...Ge contacts.

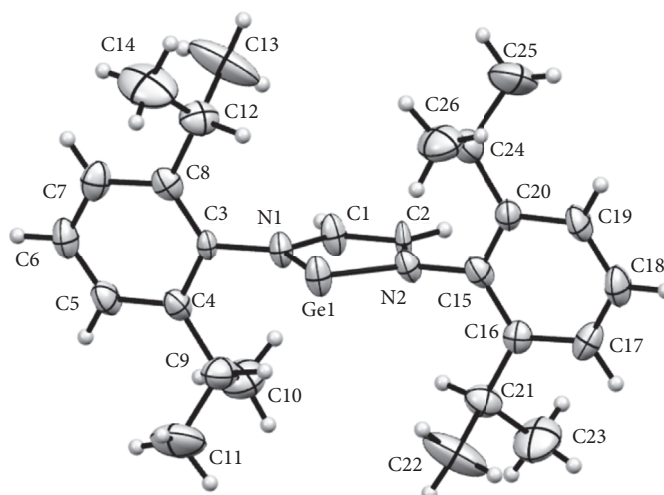


FIGURE 5: Molecular structure of the major disorder component of structure 3. Site occupancy factor 0.7688(18).

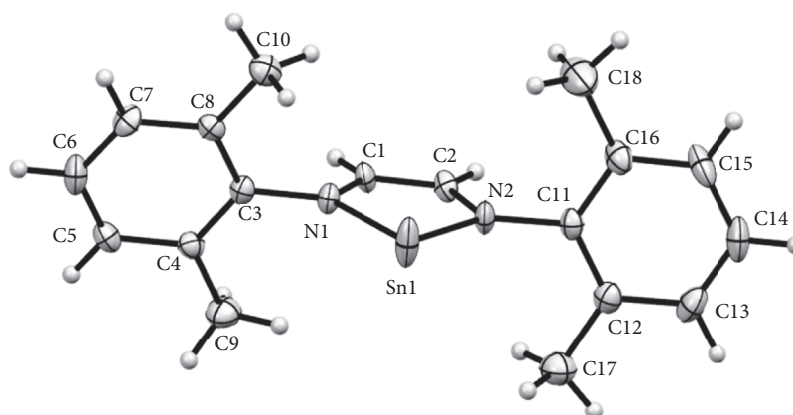


FIGURE 6: Molecular structure of the major disorder component of one of the crystallographically independent molecules found in structure 4. Site occupancy factor 0.8616(8).

metals but in the majority of cases either no reaction occurred or NHGe degradation was observed. Reaction of compound 3 with  $[\text{Au}(\text{SMe}_2)_2\text{Cl}]$  resulted in the immediate formation of a black solid and the formation of a gold mirror, suggesting that the NHGe had been subject to a degradation process. An equivalent scenario was observed when reactions were attempted with  $\text{AgBF}_4$ . The reaction of 3 with  $[\text{Ni}(\text{acac})_2]$  in THF resulted in the isolation of a sticky green solid which after the extraction into toluene/n-hexane gave green crystals. These diffracted poorly but the data obtained suggested that the NHGe had degraded and that a nickel species had formed supported by the degraded NHGe fragments. The reaction of 2 with  $[\text{Pd}(\text{PPh}_3)_4]$  was attempted, in an effort to prepare a complex with the general formula  $[\text{Pd}(\text{NHGe})(\text{PPh}_3)_n]$ . However, no reaction was observed to occur, in contrast to the reported reaction that does occur between  $[\text{Pd}(\text{PPh}_3)_4]$  and a benzoannelated N-heterocyclic plumbylene [25]. The reaction of both 1 and 2 with  $[(p\text{-cymene})\text{RuCl}_2]_2$  was attempted in THF but in both cases it was impossible to establish if the NHGe had complexed to the metal centre.  $^1\text{H}$  NMR

spectra for both of these reactions were complex while no crystals suitable for X-ray crystallography could be grown. Finally the reactions of 3 with  $\text{ZnCl}_2$  in THF and  $\text{ZnEt}_2$  in n-hexane were attempted. In each case it was established that no reaction had occurred and unreacted NHGe was recovered with confirmation provided by X-ray crystallography.

### 3. Conclusions

The synthesis of a new NHGe (compound 1) has been reported and a single-crystal X-ray diffraction study has been carried out on three NHGes (compounds 1-3). The structures of the discrete molecules are comparable with no major differences observed across the three NHGes studied. The Ge-N bond lengths were found to be in the range 1.835-1.875 Å while the N-Ge-N bond angles were between 83.6 and 85.2°. Comparison of compound 2 with the related IMes ligand revealed a significant disparity when the bond angles around the respective divalent atoms were compared. The germanium species displayed a N-Ge-N bond angle of 83.6(16)°



TABLE 2: Selected crystallographic parameters for compounds **1** to **4**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	C <sub>18</sub> H <sub>20</sub> Ge N <sub>2</sub>	C <sub>20</sub> H <sub>24</sub> Ge N <sub>2</sub>	C <sub>26</sub> H <sub>36</sub> Ge N <sub>2</sub>	C <sub>18</sub> H <sub>20</sub> Sn N <sub>2</sub>
Formula weight	336.95	365.00	449.16	383.05
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	P-1	Cc	P2 <sub>1</sub> /n
$\lambda$ Å	0.71073	0.71073	0.71073	0.71073
$a$ Å	8.1814(8)	8.1547(6)	20.1744(19)	16.8817(5)
$b$ Å	10.4765(8)	10.2887(8)	6.4753(5)	8.0981(4)
$c$ Å	11.0444(11)	12.5095(10)	20.1943(15)	18.3081(6)
$\alpha^\circ$	69.522(8)	76.744(7)	90	90
$\beta^\circ$	74.920(9)	75.010(7)	102.822(8)	96.770(3)
$\gamma^\circ$	67.374(8)	66.828(7)	90	90
Volume Å <sup>3</sup>	809.89(15)	922.40(14)	2572.3(4)	2485.44(17)
Temp. K	123(2)	123(2)	193(2)	123(2)
$Z$	2	2	4	6
$2\theta$ max°	54.0	54.0	58.1	58.9
Reflns. Collected	8394	11041 <sup>a</sup>	7323	12535
Reflns. Unique	3433	11041 <sup>a</sup>	4561	6081
Rint	0.0458	n.a. <sup>a</sup>	0.0395	0.0357
Reflns. Obs.	2663	7082	4041	4399
Goodness of Fit	1.056	0.889	1.088	1.102
R[I>2 $\sigma$ (I)], $F$	0.0451	0.0527	0.0473	0.0563
Rw, $F^2$	0.0857	0.1272	0.1227	0.0914

<sup>a</sup>This structure was found to be twinned and was refined against a hklf5 formatted reflection file. See deposited cif for further information.

which is significantly smaller than the 101.4(2)° reported for the N-C-N bond in IMes. The extended structures of compounds **1** and **2** were examined revealing some interesting differences between the intermolecular interactions that each compound exhibits. For both compounds the predominant interactions were C-H $\cdots$ C interactions between a hydrogen atom of the heterocycle and the carbon atoms of the aromatic rings. Compound **2** displays a weak interaction between the germanium atom and a hydrogen atom of a neighbouring methyl group. Similar interactions are not seen for **1**. Attempts at generating a variety of metal complexes with proligands **1**–**3** have proven unsuccessful. Given the considerable number of examples of such NHGe species, and the fact that to date only eight metal complexes have been characterised by X-ray crystallography (of which four incorporate anellated NHGe ligands and four nonanellated ligands), it is perhaps not surprising that this is the case. It has been noted from computational studies that the lone pair in these neutral five-membered N-heterocyclic germylenes is at a low energy, making them poorly nucleophilic [13], which is supported by a second study that shows the proton affinity to be one of the lowest of all NHGes [14]. These results suggest that the ligating ability of this family of NHGes is likely to be substantially poorer than their carbene analogues.

## 4. Experimental

**4.1. General Information.** All manipulations were performed under an atmosphere of N<sub>2</sub> gas using standard Schlenk

line techniques. All solvents were dried over Na wire/benzophenone and distilled/degassed prior to use. Diimine precursors [26] and SnCl<sub>2</sub>·1,4-dioxane [27] were prepared according to literature procedures while GeCl<sub>2</sub>·1,4-dioxane was purchased from Sigma-Aldrich and used without further purification.

**4.2. Spectroscopic Methods.** <sup>1</sup>H and <sup>13</sup>C NMR spectra (which are included in the supplementary materials (available here)) were recorded using either a Bruker 400 MHz spectrometer or a Bruker 600 MHz spectrometer. Elemental analyses were carried out at the University of Strathclyde.

**4.3. X-Ray Crystallography.** Measurements were made at low temperature with an Oxford Diffraction Xcalibur E instrument. Monochromated Mo ( $\lambda$  = 0.71073 Å) radiation was used for all data collections. All structures were refined to convergence against  $F^2$  and against all independent reflections using programs from the SHELX family [28]. Structure **2** was modelled as a twin. Structures **1**, **3**, and **4** were modelled with both the heavy atom and C=C parts of the heteroring disordered over two sites. For the disordered structures, geometric restraints were applied to the C-C and N-C bond lengths of the disorder components with occupancy  $\leq$  0.5 and to selected displacement parameters of the XN<sub>2</sub>C<sub>2</sub> rings (X = Ge or Sn). Selected crystallographic and refinement parameters are given in Table 2 and full data has been deposited in cif format with the CCDC as CCDC 1868443 to CCDC 1868445 for the Ge compounds **1** to **3** and as CCDC

1868574 for the Sn compound **4**. Data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**4.4. [1,3-Bis(2,6-dimethylphenyl)diazagermol-2-ylidene] (1).** Glyoxal-bis(2,6-dimethylphenyl)diimine (500 mg, 1.89 mmol) was dissolved in THF (15 mL). To this solution was added an excess of lithium metal, which had been hammered flat and cut into strips. On addition the solution changed from yellow to orange in colour. The mixture was left stirring overnight. The solution was separated from the unreacted lithium metal by cannula. To this solution was added  $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$  (438 mg, 1.89 mmol) dissolved in THF (5 mL). This resulted in the solution turning dark yellow. The volatiles were removed under vacuum and the solid residues were extracted into n-hexane (20 mL) and filtered through Celite. The resultant yellow/orange solution was concentrated in vacuo (~5 mL) and cooled to  $-18^\circ\text{C}$ . An initial crop of yellow crystals was isolated (100 mg) with a further crop of yellow powder isolated from the filtrate. Yield 200 mg, 31%. Crystals suitable for X-ray diffraction were grown by the slow cooling of a warm, concentrated solution of **1** in n-hexane.  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  = 2.22 (s, 12H,  $\text{CH}_3$ ); 6.61 (s, 2H,  $\text{C}=\text{CH}$ ); 6.96 (dd, 2H, *para*-CH,  $^3J_{\text{HH}}$  = 6.8, 1.6 Hz); 7.05 (d, 4H, *meta*-CH,  $^3J_{\text{HH}}$  = 8 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  = 18.52 ( $\text{CH}_3$ ); 125.40 ( $\text{NC}=\text{CN}$ ); 126.31 (*Ar*- $\text{C}_4$ ); 128.64 (*Ar*- $\text{C}_{3,5}$ ); 134.53 (*Ar*- $\text{C}_{2,6}$ ); 145.63 (*Ar*- $\text{C}_1$ ).  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{Ge}$ : calcd. C 64.16; H 5.94; N 8.31%; found. C 63.75; H 6.02; N 8.41%.

**4.5. [1,3-Bis(2,4,6-trimethylphenyl)diazagermol-2-ylidene] (2).** Glyoxal-bis(2,4,6-trimethylphenyl)diimine (470 mg, 1.60 mmol) was dissolved in THF (15 mL). To this solution was added an excess of lithium metal, which had been hammered flat and cut into strips. On addition the solution changed from yellow to dark orange in colour. The mixture was left stirring overnight. The solution was separated from the unreacted lithium metal by cannula. To this solution was added  $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$  (370 mg, 1.60 mmol) dissolved in THF (5 mL). This resulted in the solution turning yellow. The volatiles were removed under vacuum and the solid residues were extracted into n-hexane (15 mL) and filtered through Celite. The resultant yellow/orange solution was concentrated in vacuo (~2 mL) and cooled to  $-18^\circ\text{C}$ . A crop of orange crystals was isolated. Yield 100 mg, 17%. Crystals isolated were suitable for single-crystal X-ray diffraction study.  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  = 2.18 (s, 12H,  $\text{CH}_3$ ); 2.26 (s, 6H,  $\text{CH}_3$ ); 6.59 (s, 2H,  $\text{C}=\text{CH}$ ); 6.88 (s, 4H, *meta*-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  = 18.44 (*o*- $\text{CH}_3$ ); 21.11 (*p*- $\text{CH}_3$ ); 125.88 ( $\text{NC}=\text{CN}$ ); 129.35 (*Ar*- $\text{C}_{3,5}$ ); 134.24 (*Ar*- $\text{C}_{2,6}$ ); 135.34 (*Ar*- $\text{C}_4$ ); 143.16 (*Ar*- $\text{C}_1$ ).

**4.6. [1,3-Bis(2,6-diisopropylphenyl)diazagermol-2-ylidene] (3).** Glyoxal-bis(2,6-diisopropylphenyl)diimine (650 mg, 1.73 mmol) was dissolved in THF (20 mL). To this solution was added an excess of lithium metal, which had been

hammered flat and cut into strips. On addition the solution changed from yellow to dark orange in colour. The mixture was left stirring overnight. The solution was separated from the unreacted lithium metal by cannula. To this solution was added  $\text{GeCl}_2 \cdot 1,4\text{-dioxane}$  (440 mg, 1.90 mmol) dissolved in THF (6 mL). This resulted in the solution turning yellow. The volatiles were removed under vacuum and the solid residues were extracted into n-hexane (20 mL) and filtered through Celite. The resultant yellow/orange solution was concentrated in vacuo (~4 mL). The warmed solution was allowed to cool to room temperature slowly resulting in the isolation of pale yellow crystals. Yield 250 mg, 32%. Crystals isolated were suitable for single-crystal X-ray diffraction study.  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  = 1.20 (d, 24H,  $\text{CH}_3$ ,  $^3J_{\text{HH}}$  = 6.8 Hz); 3.06 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}}$  = 7 Hz); 6.64 (s, 2H,  $\text{C}=\text{CH}$ ); 7.16 (m, 6H, *aromatic*-CH).  $\text{C}_{26}\text{H}_{36}\text{N}_2\text{Ge}$ : calcd. C 69.57; H 8.02; N 6.24%; found. C 69.14; H 8.04; N 7.06%.

**4.7. [1,3-Bis(2,6-dimethylphenyl)diazastannol-2-ylidene] (4).** Glyoxal-bis(2,6-dimethylphenyl)diimine (1.46 g, 5 mmol), lithium metal (90 mg, 12.6 mmol), and THF (30 mL) were combined and left stirring overnight. The solution was separated from the unreacted lithium by cannula. The solution was cooled in an ice-salt bath and a solution of  $\text{SnCl}_2 \cdot 1,4\text{-dioxane}$  (1.39 g, 5 mmol) in THF (5 mL) was added dropwise. The solution darkened to a deep orange/red colour. After warming back to RT the volatiles were removed under vacuum and the solid residues were extracted into n-hexane (30 mL) and filtered through Celite. The solution was cooled to  $-18^\circ\text{C}$  overnight resulting in the precipitation of orange/red crystals alongside both pale yellow crystals and black powder. The orange/red crystals were suitable for single-crystal X-ray diffraction.

## Data Availability

Crystallographic data has been deposited in cif format with the CCDC as CCDC 1868443 to CCDC 1868445 for the Ge compounds **1** to **3** and as CCDC 1868574 for the Sn compound **4**. Data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

## Supplementary Materials

$^1\text{H NMR}$  spectra for compounds **1** to **3** and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for compounds **1** to **2**. (*Supplementary Materials*)

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